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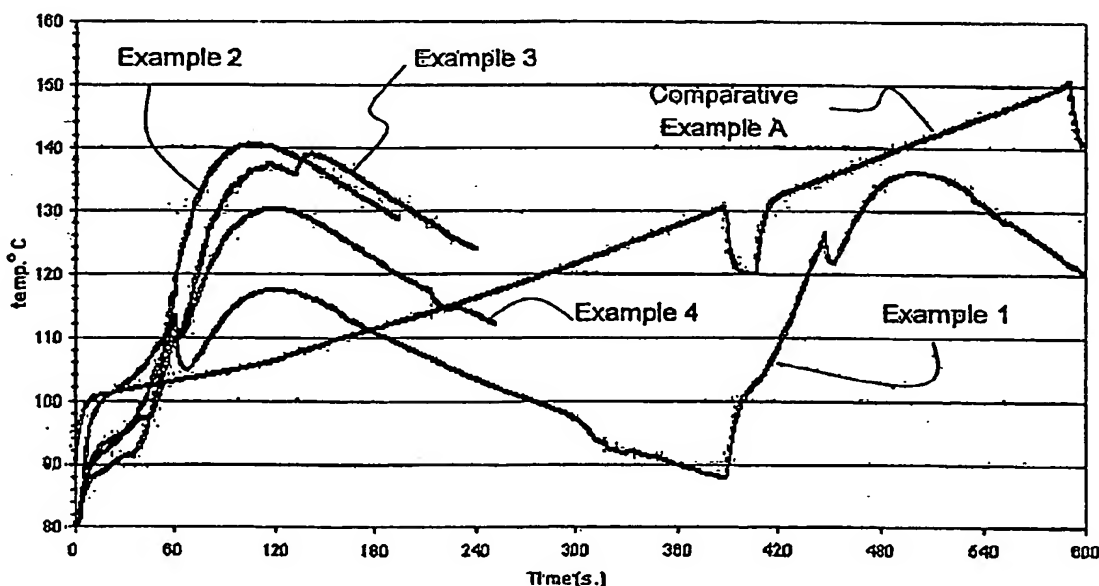
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(54) Title: **PHOTOPOLYMERIZATION OF EPISULFIDES USING METAL COMPLEXES AND ITS USE FOR MAKING OPHTHALMIC LENSES**



(57) Abstract: A process for polymerizing episulfide monomers comprising the steps of : (a) mixing to an episulfide monomer or a mixture of episulfide monomers an effective amount of at least one photopolymerization catalyst selected from the group consisting of (cyclopentadienyl) ruthenium and osmium complexes and an effective amount of at least a co-catalyst selected from phosphonium salts, phosphines and amines ; and (b) irradiating the mixture of (a) with an ultra-violet radiation to polymerize the mixture.

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PHOTOPOLYMERIZATION OF EPISULFIDES USING METAL COMPLEXES AND ITS USE FOR MAKING OPHTHALMIC LENSES

5

BACKGROUND OF THE INVENTION

The present invention concerns a method for photopolymerizing episulfides in the presence, as polymerization catalyst, of at least one metal complex, in particular a ruthenium complex, and to the use of such a photopolymerization method for making episulfide based ophthalmic lenses.

10 The use of ruthenium cyclopentadienyl complexes for anionic photopolymerization of 2-cyanoethylacrylate has been disclosed in US 5.652.280.

Thermal polymerization of episulfides is known from US 5.807.975, EP 761.665, EP 785.194 and EP 942.027. These disclosed polymerization
15 processes need long thermal polymerization cycles.

Photo-initiated cationic polymerization of monoepisulfides is disclosed in article "Photocationic cross-linking of poly(2,3-epithiopropyl methacrylate) and Photoinitiated cationic polymerization of its model compounds", M. Tsunooka et al., Journal of Polymer Science : polymer
20 chemistry edition, vol. 22, 2217-2225 (1984). However, the photoinitiators used in the polymerization are coloured materials that are not suitable for making optical lens material.

International patent application WO 00/26272 discloses a process for making thio containing resins which comprises polymerizing a composition
25 comprising at least one diepisulfide compound and, as polymerization catalyst, an alkaline metal, alkaline-earth metal or ammonium salt of an acid having a pKa from 0.5 to 14.

Although this later polymerization process leads to fast polymerization of the composition, the process is difficult to control due to
30 the highly exothermic polymerization reaction which may result in a charred resin inappropriate for making optical articles such as ophthalmic lenses.

35

BRIEF DESCRIPTION OF THE DRAWINGS

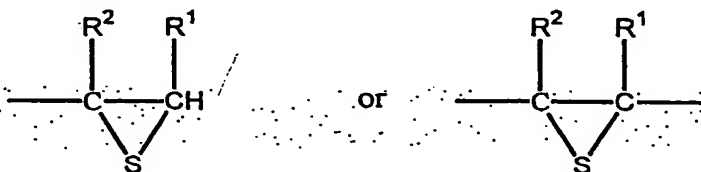
5 Figure 1 shows temperature-time graphs of the polymerization
 6 reactions for various compositions according to the invention.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

10 The episulfide compounds that can be used in the process of the invention can be mono or polyepisulfide compounds, but are preferably diepisulfide compounds.

The episulfide compounds can be defined as compounds comprising at least one episulfide functional group of formula :

15

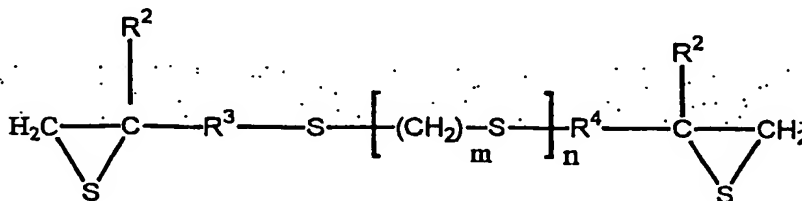


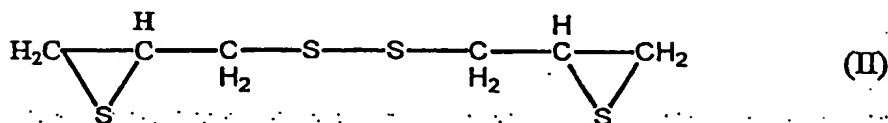
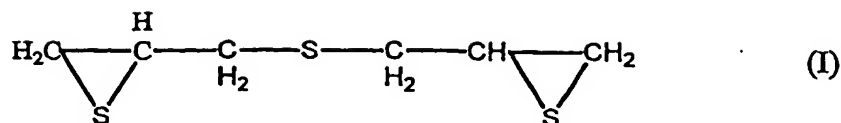
in which R¹ and R² are, independently from each other, H, alkyl, aryl,
20 alkoxy, aryloxy, alkylthio or arylthio.

The episulfide compounds may include other polymerizable functional groups such as epoxy, thiol, ethylenic such as a vinyl, (meth)acrylate, carboxylic acid or anhydride, thiocarboxylic acid, thio alcohol, thiophenol, phenol, amine or amide groups.

25 The preferred episulfide monomers are diepisulfides.

Suitable diepisulfide monomers are diepisulfides of formula :





Episulfides as defined above are disclosed in EP 761.665 and EP 942.027.

Although the polymerizable composition may only include an episulfide monomer or a mixture of different episulfide monomers as polymerizable monomers, it can also include other photopolymerizable monomers such as thiol monomers and/or (meth)acrylate monomers.

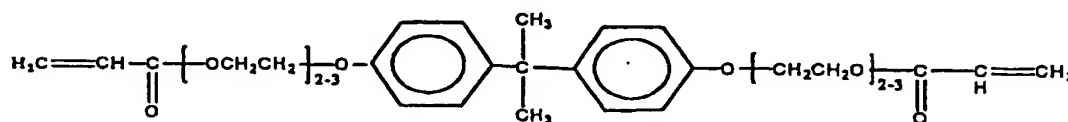
It can also include small amounts of epoxy monomers.

The (meth)acrylate monomers for use in the process of the invention can be any (meth)acrylate classically employed for making organic glass articles such as optical articles, and in particular ophthalmic lenses.

Typical examples of (meth)acrylate monomers include ethylene glycol dimethacrylate, propylene glycol dimethacrylate, tetramethylene glycol dimethacrylate, polyethylene glycol dimethacrylate, trimethylolpropane triacrylate, pentaerythritolpropane trimethacrylate, ethoxylated bisphenol-A diacrylate, 1,6-hexanediol dimethacrylate, urethane diacrylate and epoxy diacrylate.

A preferred diacrylate monomer is the diacrylate of formula :

25



The thiol monomers can be represented by formula :

30



Adding a small amount of epoxy monomer allows to use smaller amounts of ruthenium catalyst in the composition and to keep a high rate of polymerization.

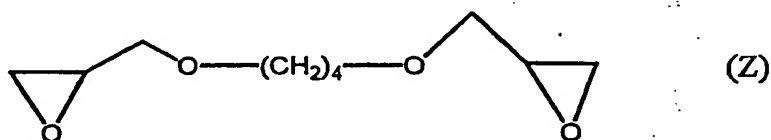
Specific epoxy compounds which may be used include, but are not limited to phenolic epoxy compounds prepared by condensation of an epihalohydrin with a polyphenol including bisphenol-A glycidyl ether ; alcoholic epoxy compounds prepared by condensation of an epihalohydrin with a polyalcohol including hydrogenated bisphenol-A glycidyl ether ; glycidyl ester epoxy compounds prepared by condensation of an epihalohydrin with an organic polyacid derivatives including 3,4-epoxycyclohexylmethyl-3',4'-epoxycyclohexane carboxylate and diglycidyl 1,2-hexahydrophthalate ; amino epoxy compounds prepared by condensation of an epihalohydrin with a secondary amine ; and aliphatic polyepoxy compounds such as vinylcyclohexene diepoxide.

Other suitable epoxy compounds are disclosed in EP 921.417 which is incorporated by reference.

Preferred epoxy compounds are those which do not contain an unsaturation and those which have two epoxy groups.

Specific suitable epoxy compounds are high refractive index epoxy compounds derived in particular from bisphenol-A or fluorene.

Another preferred epoxy compound is :



25

The photopolymerization catalyst is selected among ruthenium and osmium (cyclopentadienyl) metal complexes.

The preferred catalysts are bis(cyclopentadienyl) ruthenium complexes.

30

The metal complexes can be represented by formula :

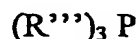
The preferred phosphonium salts can be represented by formula :



5 in which each R'' is independently an alkyl group, typically a C₁-C₆ alkyl group such as methyl, ethyl, propyl and butyl ; an alkoxy group, typically a C₁-C₆ alkoxy group such as methoxy, ethoxy and propoxy ; or aryl group, such as a phenyl group, which can be substituted with one or more alkyl groups ; and X is an anion preferably selected from the group
10 consisting of OH⁻, Br⁻, Cl⁻, I⁻, SH⁻, CN⁻, NO₂⁻, SO₂⁻ and COOH⁻, preferably Br⁻ and Cl⁻.

The most preferred phosphonium salts are tetra alkyl phosphonium bromides and chlorides and in particular tetra butyl phosphonium bromide (TBPB).

15 The preferred phosphine compounds can be represented by formula :



20 in which each R''' is independently an alkyl group, typically a C₁-C₆ alkyl group such as methyl, ethyl, propyl and butyl ; an alkoxy group, typically a C₁-C₆ alkoxy group such as methoxy, ethoxy and propoxy ; or an aryl group, such as a phenyl group, which can be substituted with one or more alkyl, alkoxy or halogeno groups.

25 The most preferred phosphines are triphenylphosphine (TPP), trimethoxyphenylphosphine (TMPP) and trichlorophenylphosphine (TCPP).

The amines can be primary, secondary or tertiary amines.

Examples of amines useful as co-catalyst in the present process are (R'')₄N⁺X⁻, (R'')₃N, (R'')₂NH and R''NH₂ in which R'' and X are as defined above.

30 The amount of co-catalyst used generally ranges from 0.005 to 1% by weight based on the total weight of the monomers and catalyst in the composition, preferably from 0.01 to 0.5%.

The polymerizable composition can include other additives typically used for making optical articles in the usual amounts, such as UV
35 stabilizers, UV absorbers, mold release agents, dyes and pigments including

for 1 to 2 hours, for example in an air-heated oven, to achieve curing of the composition.

The following examples illustrate the present invention. In the examples, unless otherwise stated all parts and percentages are by weight.

5

EXAMPLES 1 TO 7 AND COMPARATIVE EXAMPLES A AND B

Compositions containing diepisulfide monomer of formula (I), bis(cyclopentadienyl) ruthenium catalyst of formula (III) and eventually a co-catalyst were placed inside a 2mm thick, 6 base plano lens two-piece mold assembly made of mineral glass and subjected to various polymerization conditions.

10

Compositions and polymerization conditions are given in Table I below. Results are also given in Table I :

15

TABLE I

	Example n°								
	A	B	1	2	3	4	5	6	7
Composition									
Diepisulfide monomer (I) (%)	98	98	98	98	98	98	98	98	98
Ruthenium catalyst (III) (%)	2	2	2	2	2	2	2	2	2
Co-catalyst (%)									
TBPB	-	0.01	-	0.02	0.01	0.01	-	-	-
TPP	-	-	-	-	-	-	0.01	-	-
TMPP	-	-	-	-	-	-	-	0.01	-
TCPP	-	-	-	-	-	-	-	-	0.01
Pre-heating									
°C	150	115	80	80	80	80	80	80	80
UV Irradiation									
Intensity (mW/cm ²)	-	-	225	225	225	175	175	175	175
Number of shots	-	-	2	1	1	1	1	1	1
Duration of shots (D)	-	-	60/60	60	60	60	60	60	60
Gel	No	No	Yes	Yes	Yes	Yes	Yes (soft)	Yes (hard)	Yes (soft)

TABLE II

	Example n°					
	8	9	10	11	12	13
<u>Composition</u>						
Diepisulfide monomer (I) (%)	98	98	98	98	98	98
Rhutenium catalyst (III) (%)	2	2	2	2	2	2
TBPB, co-catalyst (%)	0.01	0.01	0.01	0.01	0.01	0.01
Blue dye (ppm)	-	-	0.56	0.56	1.12	2.24
<u>Pre-heating</u>						
°C	80	80	80	80	80	80
<u>UV irradiation</u>						
Intensity (mW/cm ²)	100	100	100	100	100	100
Number of shots	1	2	1	2	3	2
Duration of shots (s)	60	45/30	45	30/30	30/15/15	30/30
Gel	Yes	Yes	Yes	Yes	Yes	Yes
<u>Post-heating</u>						
°C	90	90	90	90	90	1000
Time (hours)	1,25	1,25	1,25	1,25	1,25	1,25
<u>Lens properties</u>						
% transmission	-	-	-	-	86.2	85.1
% Haze	-	-	-	-	2.11	3.19
Barcol	-	-	-	-	83.9	89.4
Yellow index	-	-	-	-	3.92	0.9

5 EXAMPLES 14 TO 16

Examples 14 to 16 describe polymerization of compositions having lower concentration of ruthenium catalyst than in preceding examples (see Table III).

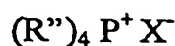
Transmission was measured using Haze-guard plus instrument. The instrument was calibrated using a standard prior to measurement with actual samples.

5 Haze was measured using Haze-guard instrument which was calibrated with a standard prior to measurement with actual samples.

Barcol was measured using Barcol instrument calibrated with a standard prior to the measurement with actual samples.

Yellow index was spectroscopically determined according to ASTM-D-1925-63.

6. The process of claim 1, wherein the phosphonium salts are salts of formula :

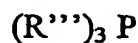


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in which each R" is independently an alkyl group, an alkoxy group or an aryl group which can be substituted with one or more alkyl and/or alkoxy groups ; and X is an anion.

7. The process of claim 1, wherein the phosphines have formula:

10



in which each R''' is independently an alkyl group, an alkoxy group or an aryl group which can be substituted with one ore more alkyl, alkoxy or halogeno groups.

8. The process of claim 1, wherein the amines are selected from amines of formula $(R'')_4N^+X^-$, $(R'')_3N$, $(R'')_2NH$ and $R''NH_2$ in which R'' is an alkyl group, an alkoxy group or an alkyl group which can be substituted with one or more alkyl and/or alkoxy groups and X is an anion.

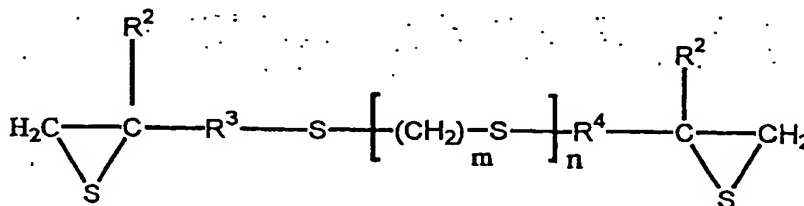
9. The process of claim 1, wherein the co-catalyst is selected from the group consisting of triphenylphosphine, trimethoxyphenylphosphine, trichlorophenylphosphine and tetrabutyl phosphonium bromide.

10. The process of claim 1, wherein the amount of co-catalyst ranges from 0.005 to 1% by weight, based on the total weight of monomers and photopolymerization catalyst.

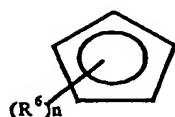
11. The process of claim 1, wherein the episulfide monomers are diepisulfide monomers.

12. The process of claim 11, wherein the diepisulfide monomers are represented by formula :

30



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M (Y)_y

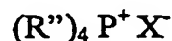
5 in which R⁵ and R⁶, independently from each other, represent a linear or branched alkyl group, an alkoxy group or an aryl group which can be substituted with one or more alkyl groups ; n is an integer from 0 to 5, M is a metal selected from Ru and Os, Y is Cl, Br, I or H, and y is an integer from 0 to 2.

10 18. The process of claim 17, wherein M is Ru.

19. The process of claim 16, wherein the photopolymerizable catalyst is bis(cyclopentadienyl) ruthenium.

15 20. The process of claim 16, wherein the amount of photopolymerization catalyst ranges from 0.1 to 10% by weight based on the total weight of monomers present in the mixture.

21. The process of claim 16, wherein the phosphonium salts are salts of formula :

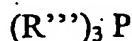


20

in which each R'' is independently an alkyl group, an alkoxy group or an aryl group which can be substituted with one or more alkyl groups ; and X is an anion.

22. The process of claim 16, wherein the phosphines have formula :

25



28. The process of claim 26, wherein the diepisulfide monomer is bis-2,3-(epithiopropyl)sulfide or bis-2,3-(epithiopropyl)disulfide.

29. The process of claim 16, wherein the mixture of step (a) further comprises one or more photopolymerizable monomers selected from polythiol monomers, (meth)acrylate monomers, and epoxy monomers.

30. The process of claim 29, wherein the epoxy monomer is present at a ratio of 10% or less based on the total weight of the monomers in the composition.

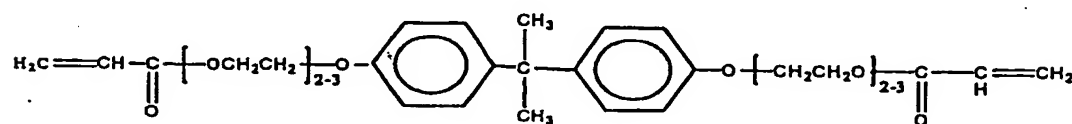
31. The process of claim 29, wherein the polythiol monomers are represented by formula :



In which n' is an integer from 2 to 6 and R' is an organic group of valency equal to n' .

32. The process of claim 29, wherein the (meth)acrylate monomers are selected from the group consisting of ethylene glycol dimethacrylate, propylene glycol dimethacrylate, tetramethylene glycol dimethacrylate, polyethylene glycol dimethacrylate, trimethylolpropane triacrylate, pentaerythritolpropane trimethacrylate, ethoxylated bisphenol-A diacrylate, 1,6-hexanediol dimethacrylate, urethane diacrylate and epoxy diacrylate.

33. The process of claim 23, wherein the (meth)acrylate monomer is represented by formula :



34. The process of claim 16, wherein the post-heating step comprises heating the gel for 1 to 2 hours at a temperature ranging from 80 to 120°C.

35. The process of claim 16, further comprising prior to step (b) a pre-heating step of the mixture of step (a) to a temperature of 70°C to 90°C.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP 02/04752

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C08G75/08

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C08G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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Y	EP 1 006 374 A (MITSUBISHI GAS CHEMICAL CO) 7 June 2000 (2000-06-07) page 2, line 30 -page 3, line 20 page 5, line 9 -page 7, line 9 page 9, line 30 -page 11, line 18 claims 1-8 ---	1-35
Y	EP 0 896 974 A (MINNESOTA MINING & MFG) 17 February 1999 (1999-02-17) page 3, line 17 -page 4, line 18 page 4, line 28 -page 5, line 33 claims 1-3 --- -/-	1-35

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☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

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